

钙钛矿氧化物催化氧化VOCs的研究进展

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摘要

钙钛矿氧化物(ABO_3)催化剂具有高活性和热稳定性, 以及可调节的元素组成和可调控的氧化还原性质, 使其性能得到改善, 因此是VOCs催化氧化领域最具竞争力的材料之一。尽管 ABO_3 催化剂具有广泛的应用潜力, 但其使用受到失活和烧结敏感性的限制, 这可能会影响其长期性能, 从而限制其在工业中的使用。本文从非掺杂、掺杂(A位点、B位点和A/B位点掺杂)和负载型 ABO_3 三个方面总结了当前研究的相关进展。与非掺杂 ABO_3 氧化物相比, 掺杂型催化剂表现出更高的活性和稳定性。此外, 本文提出了 ABO_3 氧化物催化氧化VOCs存在的三种机理。最后, 对 ABO_3 催化剂催化VOCs燃烧的问题及展望进行了探讨, 为进一步设计新型高效低温催化剂提供了思路。

关键词

钙钛矿氧化物, 催化氧化, 挥发性有机物, 反应机理

Recent Advances in Catalytic Oxidation of VOCs Using Perovskite Oxide

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Abstract

Perovskite oxide (ABO_3) catalysts are among the most competitive substances in the domain of volatile organic compounds (VOCs) catalytic oxidation because of their high activity, thermal stability, adjustable elemental composition and flexible structure. Despite the broad range of potential

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applications of ABO_3 catalysts, their utilization is constrained by inactivation and sintering susceptibility, which could impact their long-term performance and thereby limit their application in industry. In this article, the contemporary research progress is summarized from three aspects: non-doping, doping (doping at A site, B site and A/B site) and supported ABO_3 . Compared with undoped ABO_3 oxides, doped catalysts demonstrated higher activity and stability. Three mechanisms of VOCs catalytic oxidation were put forward. Ultimately, the problems and prospects of VOCs combustion catalyzed by ABO_3 catalysts were discussed, which provided insights for the further design of new high-efficiency and low-temperature catalysts.

Keywords

Perovskite Oxides, Catalytic Oxidation, Volatile Organic Compounds, Reaction Mechanism

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1. 引言

挥发性有机化合物(VOCs)是一种在室温和大气压下的沸点为 $50^\circ\text{C}\sim 260^\circ\text{C}$ 的空气污染物,对自然环境具有严重威胁[1]。VOCs 排放后与氮氧化物等其他气体反应,会形成二次污染物,产生臭氧和 $\text{PM}_{2.5}$ (直径通常为 $2.5\ \mu\text{m}$ 及以下的可吸入颗粒物),对空气质量造成负面影响[2]。此外,部分 VOCs 还会参与化学反应,破坏大气中的臭氧层,增加紫外线的穿透量,加剧全球变暖问题。除了是臭氧、 $\text{PM}_{2.5}$ 等污染物的常见前体外, VOCs 对人类构成严重的健康风险,具有致癌性和致畸性[3]。随着工业化和经济增长的加速,近年来中国挥发性有机化合物的年排放量急剧增加。例如,2015 年中国的挥发性有机化合物排放量接近 3112 万吨[4]。如图 1 所示,工业生产(石化、化学工程、涂料和印刷)占当年中国挥发性有机化合物人为来源的 43%。由于挥发性有机化合物对环境和人类健康的极端不利影响,以及挥发性有机化合物排放量的不断增长,世界各国政府制定了越来越严格的排放标准来限制各行各业产生的挥发性有机化合物[5]。因此,在工业和研究领域,通过开发实用的环境修复工具和技术来有效去除挥发性有机化合物面临着巨大的挑战。

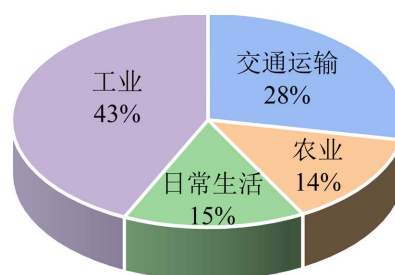


Figure 1. Classification of VOCs degradation method

图 1. 2015 年中国不同来源的 VOCs 排放

根据生产原理和理化性质, VOCs 减排技术分为两大类。一是回收浓缩技术,目前最常用的技术有吸附[6]、膜分离[7]和冷凝[8]。二是降解技术,包括直接焚烧[9]、催化氧化[10]和生物降解[11]。由于回收浓缩技术不能直接降解 VOCs,并且具有处理过程繁杂,处理成本高,效率低,还可能会造成二次污染等缺点,从而限制了回收浓缩技术的应用[12]-[14]。直接焚烧可以处理大多数挥发性有机化合物,但不完全

的热燃烧会在焚烧炉烟气中产生不需要的副产物,如二噁英和一氧化碳[15]。生物处理具有特异性高、降解时间长、降解效率低等缺点,因此限制了其广泛应用[4]。相比之下,催化氧化能够在相对较低的温度(200℃~500℃)下完全转化 VOCs,并且在最佳催化条件下,VOCs 可以完全矿化为无毒无害的 CO₂ 和 H₂O,因此催化氧化法被认为是去除 VOCs 的最有效方法[16]。

稳定高效的催化剂是催化燃烧的核心。已经报道了各种催化剂,包括贵金属基和非贵金属氧化物催化剂。贵金属催化剂具有低温活性好、稳定性高、耐腐蚀、再生性能好、选择性高等优点[17],但由于贵金属催化剂价格相对昂贵且容易因烧结或中毒而失活的缺点,极大地限制了其实际应用[18]。非贵金属催化剂因其表面积大、成本低、来源广、易于合成、抗毒性高等优点而被广泛应用[19]。在非贵金属催化剂体系中,钙钛矿氧化物因其低温下具有高活性、高稳定性和易于调节的氧化还原特性而备受关注[20][21]。与许多贵金属基催化剂相比,钙钛矿氧化物具有较大的比表面积,使其具有高活性和成本效益[22]。金属氧化物钙钛矿遵循通式 ABO₃,其中 A 代表稀土(La³⁺、Sr²⁺、Ce⁴⁺、Sm²⁺、Gd²⁺等)、碱金属离子(K⁺、Rb⁺、Cs⁺等)或碱土离子(Be²⁺、Mg²⁺、Ca²⁺、Ba²⁺等),B 代表过渡金属离子(Co²⁺、Mn³⁺、Ni³⁺和 Fe²⁺等)[23]。ABO₃ 的三种典型结构如图 2。值得注意的是,用具有相似半径的阳离子取代 A 位或 B 位点的阳离子可以产生缺陷和氧空位以提高催化性能[24]。本文综述了 ABO₃ 基催化剂催化氧化 VOCs 的最新进展,评估了 ABO₃ 的催化性能,包括非掺杂、掺杂(A 位点、B 位点和 A/B 位点掺杂)和负载型 ABO₃,总结了 VOCs 可能的氧化机理。

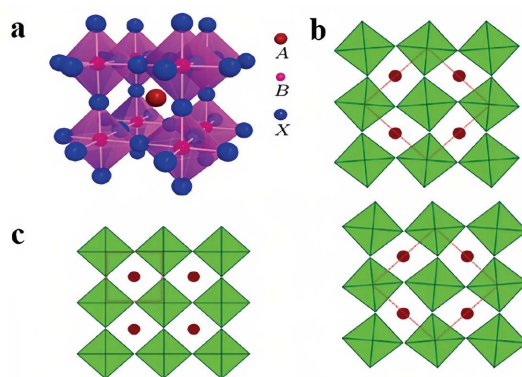


Figure 2. Three typical structures of ABO₃-type perovskites
图 2. 型钙钛矿的三种典型结构

2. 钙钛矿氧化物催化氧化 VOCs

2.1. 非掺杂型钙钛矿氧化物

在非掺杂型钙钛矿,La 基 ABO₃ 因其结构稳定性和成分多功能性而被广泛研究。La 基 ABO₃ 是各种反应的优良催化剂,主要用于醛和酮的还原,但也用于 VOCs 的氧化。Spinicci 等人研究了使用 LaMnO₃ 和 LaCoO₃ 氧化苯的过程,前者具有更高的活性(T_{50%}相差 20℃)。氧化还原分析证实,LaCoO₃ 中的 Co 完全处于 Co³⁺,而 LaMnO₃ 除了 Mn³⁺ 外还含有 35%的 Mn⁴⁺。因此,B 位点的金属离子和价态对催化性能有显著影响[25]。Liu 等人使用柠檬酸溶胶凝胶(SG)、自熔聚合(SMP)、浸渍(IM)和共沉淀(CP)技术合成了 SmMnO₃ (SMO),并将钙钛矿应用于甲苯的氧化,催化剂活性遵循 SMO-SMP > SMO-SG > SMO-IM > SMO-CP 趋势,与催化剂的比表面积和表面吸附氧的浓度一致[26]。Rezlescu 等人比较了使用溶胶-凝胶自燃法制备的 GdAlO₃、SrMnO₃、SrCoO₃ 和 MnFeO₃ 完全催化氧化苯的活性,SrMnO₃ 在低温下表现出最高的催化活性。催化活性的差异归因于所涉及的物种的不同反应性和钙钛矿表面活性位点数量的变化[27]。使用酸或碱溶液去除 A 位阳离子可以选择性地暴露额外的 B 位点并增加其表面积,进而增强其活

性, Si 等采用硝酸选择性地去除 LaMnO_3 中过量的 La, 并分析其催化功能。酸处理导致 La/Mn 降低, $\text{Mn}^{4+}/\text{Mn}^{3+}$ 增高, 表面晶格氧和吸附氧($\text{O}_{\text{latt}}/\text{O}_{\text{ads}}$)的比例增加, 这些变化丰富了氧物种并提高了晶格氧迁移率, 使得钙钛矿催化剂催化氧化性能 VOCs 性能显著提高[28]。如图 3 所示, Li 等利用酸性高锰酸钾对催化剂表面进行处理, 使 LaMnO_3 暴露了更多的 B 位点, 促进了 B 位点的 Mn^{3+} 氧化为 Mn^{4+} 。该催化剂对甲苯的低温活性进行评估发现, $\text{MnO}_2/\text{LaMnO}_3$ 在 234°C 下去除甲苯的效率为 90%。样品显示出更大的氧空位密度和更多的 Mn^{4+} 含量, 这是其高活性的根本原因[29]。表 1 概述了过去二十年中非掺杂型 ABO_3 化合物催化氧化甲苯的性能评估。 LaCoO_3 、 LaMnO_3 和 LaFeO_3 已被广泛研究, 其他非掺杂 ABO_3 物种的进一步开发似乎值得进一步开发。从表 1 可以看出, 非掺杂型 ABO_3 的转化温度和性能各不相同, 主要受风速、苯和甲苯浓度以及其他反应条件的影响。

Table 1. Non-doped ABO_3 evaluated in the catalytic oxidation of toluene
表 1. 非掺杂型 ABO_3 催化氧化甲苯性能

Samples	Conc.(ppm)	WHSV/(mL/(g·h))	T50% ($^\circ\text{C}$)	T90% ($^\circ\text{C}$)	Ref.
SmMnO_3	1000	48,000	223	258	[26]
LaFeO_3	1000	20,000	—	243	[27]
LaFeO_3	1000	20,000	308.1	333.3	[30]
LaCoO_3	500	19,200	—	275	[31]
LaNiO_3	4000	47,000	297	—	[32]
$\text{LaMnO}_3\text{-SG}$	1000	15,000	204	224	[33]
$\text{LaMnO}_3\text{-GC}$	1000	15,000	245	274	[33]
$\text{LaMnO}_3\text{-CP}$	1000	15,000	214	257	[33]
LaMnO_3	1000	60,000	229	298	[34]
SmMnO_3	1000	24,000	—	<240	[35]
GdMnO_3	1000	60,000	244	276	[36]
LaCrO_3	1000	9600	352	445	[37]

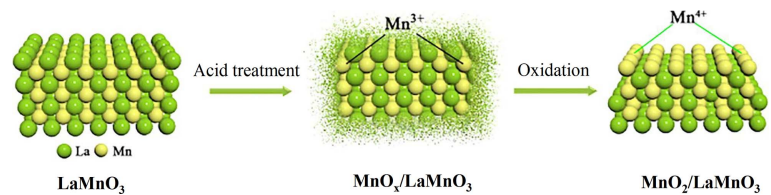


Figure 3. Synthetic route of the $\text{MnO}_2/\text{LaMnO}_3$ sample
图 3. $\text{MnO}_2/\text{LaMnO}_3$ 样品的合成路线

2.2. 掺杂型钙钛矿氧化物

可以通过半径相似的离子替代 A、B 和 O 位点的阳离子来达到提高催化剂催化活性的目的[38]。催化活性主要归因于 B 位阳离子, A 位阳离子起稳定催化剂结构的作用[39]。然而, 用其他金属离子取代 A 位阳离子可能会导致 B 位阳离子的氧化态、氧空位和阳离子缺陷密度的改变, 最终影响催化性能。因此, ABO_3 的催化活性可以通过部分或同时取代 A 和 B 位点阳离子来改变[40]。表 2 总结了在 VOCs 催化氧化中评估的所有掺杂型 ABO_3 。

Table 2. Doped ABO₃ evaluated in the catalytic oxidation of toluene**表 2.** 掺杂型 ABO₃ 催化氧化甲苯性能

Samples	Conc.(ppm)	WHSV/(mL/(g·h))	T _{50%} (°C)	T _{90%} (°C)	Ref.
La _{0.8} Sr _{0.2} MnO _{3-δ}	500	20,000	520	-	[80]
La _{0.8} Ca _{0.2} FeO ₃	4000	47,000	289	-	[32]
La _{0.8} Ca _{0.2} NiO ₃	4000	47,000	333	-	[32]
La _{0.67} Ca _{0.33} CrO ₃	1000	9600	302	381	[37]
La _{0.8} Ca _{0.2} CrO ₃	1000	9600	354	424	[37]
La _{0.5} Ca _{0.5} CrO ₃	1000	9600	295	374	[37]
La _{1-x} Ce _x MnO ₃	1000	60,000	-	450	[81]
LaNi _{0.75} Co _{0.25} O ₃	1000	18,000	-	225	[63]
La _{0.5} Sr _{0.5} Co _{0.8} Fe _{0.2} O _{3-δ}	1000	30,000	251	270	[79]
La _{0.8} Ce _{0.2} Mn _{0.8} Ni _{0.2} O ₃	1000	18,000	-	295	[72]
La _{0.7} Sr _{0.3} Co _{0.8} Fe _{0.2} O ₃	500	5700	>243	-	[74]
La _{0.9} Sr _{0.1} Mn _{0.9} Fe _{0.1} O ₃	500	30,000	213	236	[77]
La _{0.8} Ce _{0.2} Mn _{0.3} Fe _{0.7} O ₃	1000	6000	179	202	[82]
La _{0.6} Ce _{0.4} Co _{0.6} Fe _{0.4} O ₃	1000	60,000	190	318	[59]
La _{0.95} Ag _{0.05} CoO ₃	1000	30,000	238	268	[47]

2.2.1. A 位阳离子掺杂

ABO₃ 的 A 位离子通过控制活性 B 位组分的分散状态和原子价, 在稳定结构方面起着关键作用。尽管 A 位离子很少直接参与化学反应, 但 A 位离子的取代间接影响 B 位离子的价态[41]。它们还可以引入晶格缺陷并修饰晶格氧的化学位点, 从而影响 B 位的反应性[42]。

不同 Sr 掺杂的 La_{1-x}Sr_xMnO₃ (x = 0, 0.1, 0.2) 钙钛矿氧化物有效地提高了甲烷氧化的催化性能, 并通过在催化剂表面形成稳定的硫酸盐来增强硫耐受性, La_{0.8}Sr_{0.2}MnO₃ 催化剂的催化性能最好[43]。同样, 采用溶胶-凝胶法合成了 Sr 掺杂的 LaMnO₃ 钙钛矿催化剂, 由于其在较高 Mn⁴⁺ 浓度下具有更高的氧活化能力和更好的氧化还原性能, 因而作为氯乙烯燃烧的有效催化剂。另外, 碱性较强的 Sr 离子倾向于形成 Sr-Cl 键, 保持活性 Mn 物种不含氯[44]。Ce 掺杂的 La_{1-x}Ce_xMnO₃ (x = 0~0.5) 钙钛矿有效地用于苯乙烯氧化, 并且由于 Mn 离子的化合价和表面积的变化, 催化活性增加[45]。另一种 A 位掺杂的 La_{0.8}A_{0.2}MnO₃ (A = Mg, Ce, Sr) 用于氯乙烯催化氧化, La_{0.8}Ce_{0.2}MnO₃ 由于在这种较大的催化剂表面上具有更多的吸附氧而显示出最高的活性[46]。钙钛矿催化剂通过在催化剂中引入贵金属, 有效地增强了钙钛矿催化剂对 VOCs 催化氧化的活性, 许多研究都在钙钛矿的 A 位掺杂贵金属。溶胶-凝胶法合成的 Ag 掺杂的 La_{1-x}Ag_xCoO₃ (x = 0~0.05) 钙钛矿比浸渍法制备的催化剂对甲苯具有更好的氧化活性[47]。另一种 Ag 掺杂的 La_{1-x}Ag_xFeO₃ (x = 0~0.25) 钙钛矿被用作甲烷和己烷氧化催化剂, 掺杂 x ≥ 0.05 时, 甲烷氧化活性更高, 而掺杂 x ≥ 0.1 时, 己烷氧化活性最高[48]。由于电子性质的改变, Ca²⁺ 取代的 LaFeO₃ 和 LaNiO₃ 对乙醇和乙酸乙酯燃烧的催化活性有了显著提高[49]。同样, 由于晶体结构的改变, Ca²⁺ 掺杂的 LaCoO₃ 也显示出更好的丙烷氧化活性[50]。同样的结果也被发现用于甲苯氧化的 La_{1-x}Ca_xCoO₃ 催化剂和 1,2-二氯乙烷氧化的 La_{0.8}Al_{0.2}MnO₃ 催化剂[51] [52]。通过溶胶-凝胶法合成了 SmMnO₃、Sm_{0.8}A_{0.2}MnO₃ (A = Ce、Sr 和 Ca) 和 Sm_{1-x}Ca_xMnO₃ (x = 0.0, 0.1, 0.2, 0.3), 并在固定床反应器中评估甲苯的催化氧化。Ce⁴⁺ 和 Ca²⁺ 的取代对甲苯氧化的催化性能有积极影响, 而 Sr²⁺ 的取代则有负面影响(图 4(a)) [53]。Zhao 等人制备了 A 位取代

$\text{La}_{0.6}\text{Sr}_{0.4}\text{FeO}_{3-\delta}$ 在甲苯氧化中表现出优异的催化性能($T_{10\%} = 54^\circ\text{C}$, $T_{50\%} = 225^\circ\text{C}$, $T_{90\%} = 280^\circ\text{C}$) [54]。 $\text{La}_{0.6}\text{Sr}_{0.4}\text{FeO}_{3-\delta}$ 催化剂的高性能(图 4(b))与其较大的比表面积有关。受这项工作的启发, Ji 等人用 Eu^{2+} 代替了 Sr^{2+} , 得到了 $\text{Eu}_{1-x}\text{Sr}_x\text{FeO}_3$ ($x = 0$ 和 0.4), 其显示出更高的表面氧浓度和更好的甲苯氧化活性(图 4(c)) [55]。Heidinger 等人探索了 Sr^{2+} 和 Ce^{4+} 取代 LaCoO_3 对甲苯的氧化性能, Sr^{2+} 取代 LaCoO_3 显著改变了 Co^{3+} 的还原和氧解吸性能, 催化剂的稳定性得到改善, 而 Ce^{4+} 取代的影响有限(图 4(d)) [56]。

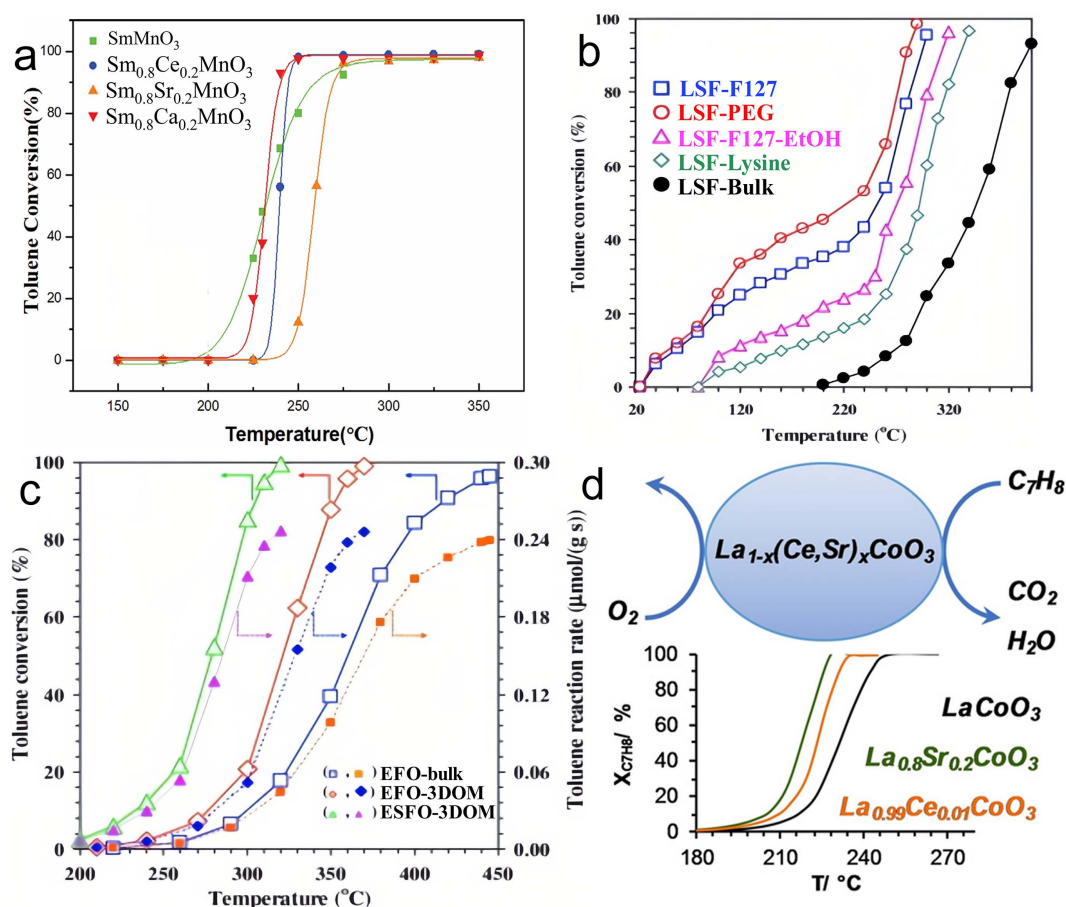


Figure 4. (a) Performance of $\text{Sm}_x\text{A}_{1-x}\text{MnO}_3$ ($A = \text{Ce, Sr, and Ca}$) perovskite for efficient catalytic oxidation of toluene; (b) Toluene conversion of the $\text{La}_{0.6}\text{Sr}_{0.4}\text{FeO}_{3-\delta}$ catalysts; (c) Toluene conversion and the corresponding reaction rate versus reaction temperature catalyzed by $\text{Eu}_{1-x}\text{Sr}_x\text{FeO}_3$ -bulk, 3D ordered macroporous materials (3DOMs) $\text{Eu}_{1-x}\text{Sr}_x\text{FeO}_3$, and 3DOM $\text{Eu}_{1-x}\text{Sr}_x\text{FeO}_3$ catalysts; (d) La (Sr and Ce) CoO_3 and their properties in toluene catalytic total oxidation

图 4. (a) $\text{Sm}_x\text{A}_{1-x}\text{MnO}_3$ ($A = \text{Ce, Sr, Ca}$) 钙钛矿对甲苯的高效催化氧化性能; (b) $\text{La}_{0.6}\text{Sr}_{0.4}\text{FeO}_{3-\delta}$ 催化甲苯转化率; (c) $\text{Eu}_{1-x}\text{Sr}_x\text{FeO}_3$ 块体、3D 有序大孔材料(3DOM) $\text{Eu}_{1-x}\text{Sr}_x\text{FeO}_3$ 和 3DOM $\text{Eu}_{1-x}\text{Sr}_x\text{FeO}_3$ 催化剂催化甲苯转化率及其反应速率与反应温度的关系; (d) La (Sr 和 Ce) CoO_3 及其在甲苯催化全氧化中的性能

2.2.2. B 位阳离子掺杂

钙钛矿的物理性质和稳定性主要取决于 B 位金属离子, B 位金属离子对 VOCs 去除的催化效率也有很大影响。因此, 一些研究人员试图通过在 B 位掺杂具有不同氧化态的过渡金属(Fe 、 Mn 、 Cu 、 Ni 和 Co) 来提高钙钛矿催化剂去除 VOCs 的催化效率。此外, 与 A 位点离子相比, ABO_3 中的 B 位点取代更加复杂, 其催化活性由 B 位点过量金属阳离子的性质决定[57]。B 位过渡金属离子表现出广泛的氧化态, 增加了其取代效应的复杂性, 超过了 A 位离子[58]。

使用热液合成的 $\text{SrTi}_{0.86}\text{Mn}_{0.14}\text{O}_3$ 和 $\text{SrTi}_{0.89}\text{Cu}_{0.11}\text{O}_3$ 进行甲苯氧化, 结果表明, 由于表面吸附氧和晶格氧($\text{O}_{\text{ads}}/\text{O}_{\text{latt}}$)的比例增加, 在 Mn 掺杂的情况下, 催化活性增加[59]。Alvarez-Galvan 等报道, LaBO_3 ($\text{B} = \text{Ni}, \text{Co}, \text{Cr}, \text{Mn}$)钙钛矿可有效用于甲基乙基酮(MEK)氧化, Mn 和 Co 是作为替换离子首选[60]。Hosseini 等人合成了纳米结构的 LaFeO_3 和 $\text{LaZn}_x\text{Fe}_{1-x}\text{O}_3$ ($x = 0.01, 0.05, 0.1, 0.2, 0.3$)钙钛矿, 并评估了它们在甲苯的催化氧化中的作用(图 5(a))。表征数据显示, 当 $x \leq 0.1$ 时, Zn 完全插入到 LaFeO_3 中。但在 $x > 0.1$ 时, ZnO 发生了一定程度的偏析。催化活性随着 Zn 含量的增加而增加, 部分原因是 ZnO 的存在, ZnO 的比例影响催化剂的氧活化能力和反应活性[61]。Lv 等人研究了 $\text{LaCo}_{1-x}\text{M}_x\text{O}_3$ ($\text{M} = \text{Fe}, \text{Cr}$ 和 Cu)在相同条件下的催化性能, 并观察到在 ABO_3 的 B 位点引入适当比例的特定金属阳离子可以提高催化活性, 主要是通过改变 B 位点阳离子的价态和氧空位含量(图 5(b), 图 5(c)) [62]。Qi 发现在 LaNiO_3 的 B 位点掺杂少量 Co_{3+} 显著增强了甲苯的催化氧化性能, 而用 Cu^{2+} 取代 Ni^{3+} 并没有提高活性(图 5(d)、图 5(e))。在所有测试的催化剂中, $\text{LaNi}_{0.75}\text{Co}_{0.25}\text{O}_3$ 表现出最高的活性, 能够在相对较低的温度($T_{90\%} = 225^\circ\text{C}$)下进行甲苯氧化[63]。

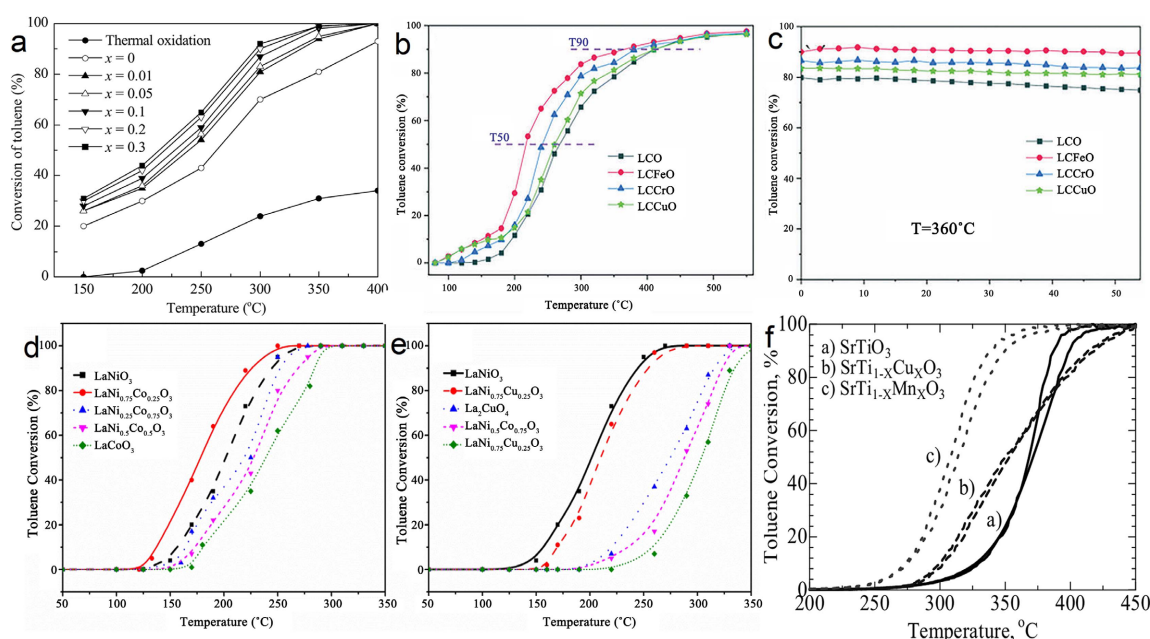


Figure 5. (a) Performance of LaMnO_3 perovskites in the catalytic oxidation of toluene; (b), (c) Catalytic performance of $\text{LaCo}_{1-x}\text{M}_x\text{O}_3$ ($\text{M} = \text{Fe}, \text{Cr}$ and Cu), $\text{LaNi}_x\text{B}_{1-x}\text{O}_3$ ($\text{B} = \text{Co}$ and Cu); (d) (e) LaMnO_3 ($\text{B} = \text{Co}$ and Cu); (f) Catalytic oxidation of toluene using $\text{SrTi}_{1-x}\text{B}_x\text{O}_3$ ($\text{B} = \text{Cu}$ and Mn)

图 5. (a) LaMnO_3 钙钛矿在甲苯催化氧化中的性能; (b) (c) $\text{LaCo}_{1-x}\text{M}_x\text{O}_3$ ($\text{M} = \text{Fe}, \text{Cr}$ 和 Cu), $\text{LaNi}_x\text{B}_{1-x}\text{O}_3$ ($\text{B} = \text{Co}$ 和 Cu) 的催化性能; (d) (e) LaMnO_3 ($\text{B} = \text{Co}$ 和 Cu); (f) $\text{SrTi}_{1-x}\text{B}_x\text{O}_3$ ($\text{B} = \text{Cu}$ 和 Mn) 催化氧化甲苯

除催化活性外, B 位阳离子还与钙钛矿的耐久性和对杂质(潜在催化剂毒物)的耐受性密切相关。Vazquez 等人探讨了 SrTiO_3 中 B 位阳离子对甲苯催化氧化性能的影响(图 5(f)) [64]。金属掺杂剂的添加确保了在三个催化循环和寿命测试中具有良好的稳定性。然而, 在掺杂 Cu 的催化剂表面观察到 CuO 沉积。将 Mn^{4+} 掺入 SrTiO_3 的 Ti^{4+} 位点可提高 $\text{O}_{\text{ads}}/\text{O}_{\text{latt}}$ 的比值和催化性能。值得注意的是, 在 350°C 以下的温度下, 掺杂 Mn^{4+} 和 Cu^{2+} 的 $\text{SrTi}_{1-x}\text{B}_x\text{O}_3$ 对甲苯完全转化为 CO_2 的催化活性最高。Zhang 等研究了 B 位点掺杂的 $\text{LaB}_{0.2}\text{Mn}_{0.8}\text{O}_3$ ($\text{B} = \text{Fe}, \text{Ni}, \text{Co}$)钙钛矿对氯乙烯氧化的作用, 结果表明, Ni 掺杂催化剂具有最高的氧迁移率、还原性和催化活性[65]。一些非金属元素也被用作钙钛矿结构稳定性和导电性提高的掺杂剂[66]。定量($x = 0.03$)的磷掺杂 $\text{LaCo}_{1-x}\text{P}_x\text{O}_3$ ($x = 0 \sim 0.05$)催化剂通过增加表面活性氧有效地提高了丙烷催化氧化的

效率[67]。Zheng 等报道, B 掺杂的 $\text{LaCo}_{0.93}\text{B}_{0.07}\text{O}_3$ 钙钛矿由于存在更多的活性位点和更好的还原性, 对氧化丙烷表现出最佳的催化性能[68]。有趣的是, 这种非金属掺杂钙钛矿催化剂具有出色的热稳定性, 可用于工业上 VOCs 燃烧。

2.2.3. A/B 位阳离子掺杂

A 位点和 B 位点同时掺杂或共掺杂方法也被广泛用于制备有效的钙钛矿作为去除 VOCs 的催化剂。 ABO_3 的 A 位阳离子间接影响 B 位离子的价态和催化剂内的氧空位, 导致 B 位离子的电子态和 B-O 键长的变化, 其中 B 位点阳离子在氧化反应中起活性催化中心的作用[69] [70]。此外, 共掺杂可以同时实现 ABO_3 的结构和电子性能的调控。因此, 可以采用 A 位点和 B 位点离子的部分取代来改善 ABO_3 的催化性能[71]。Yuan 等人研究了 $\text{La}_{1-x}\text{Ce}_x\text{Mn}_{1-y}\text{Ni}_y\text{O}_3$ 钙钛矿中掺杂 Ce^{4+} 和 Ni^{3+} 对催化甲苯氧化的影响, 其中 $\text{La}_{0.8}\text{Ce}_{0.2}\text{Mn}_{0.8}\text{Ni}_{0.2}\text{O}_3$ 对甲苯氧化的转化率最高(图 6(a)、图 6(b)) [72]。XPS 分析表明, $\text{La}_{0.8}\text{Ce}_{0.2}\text{Mn}_{0.8}\text{Ni}_{0.2}\text{O}_3$ 具有较高的晶格氧含量以及较低的氧化还原起始温度, 都有助于甲苯的催化氧化(图 6(c)~(e))。A 位 Ce 和 B 位 Ni 共掺杂 $\text{La}_{0.8}\text{Ce}_{0.2}\text{Mn}_{0.8}\text{Ni}_{0.2}\text{O}_3$ 催化剂由于比表面积、 $\text{Mn}^{4+}/\text{Mn}^{3+}$ 比和活性氧含量的增大, 对三氯乙烯(TCE)表现出最高的催化活性[73]。同样, $\text{La}_{0.7}\text{Sr}_{0.3}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_3$ 钙钛矿由于形态变化和粒径减小而显示出显著增加的甲苯氧化活性[74]。Deng 等报道了 Ce、Fe 共掺杂 $\text{La}_{1-y}\text{Ce}_y\text{Co}_{1-x}\text{Fe}_x\text{O}_3$ ($x = 0 \sim 1.0$; $y = 0 \sim 0.1$) 催化剂, 用于 CH_3OH 和 CH_4 氧化[75]。对水热法制备的 $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{1-y}\text{Fe}_y\text{O}_3$ 和 $\text{La}_{0.6}\text{Sr}_{0.4}\text{Mn}_{1-y}\text{Fe}_y\text{O}_3$ ($y = 0, 0.1, 1.0$) 进行甲苯氧化测试, 发现 $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.9}\text{Fe}_{0.1}\text{O}_3$ 通过形成 $\text{Fe}^{3+}\text{-O-Fe}^{4+}$ 表现出最高的活性[76]。 Fe^{3+} 和 Sr^{2+} 共掺杂 $\text{La}_{0.9}\text{Sr}_{0.1}\text{Mn}_{0.9}\text{Fe}_{0.1}\text{O}_3$ 催化剂的 LaMnO_3 表现出与某些贵金属基催化剂相似的甲苯氧化活性[77]。

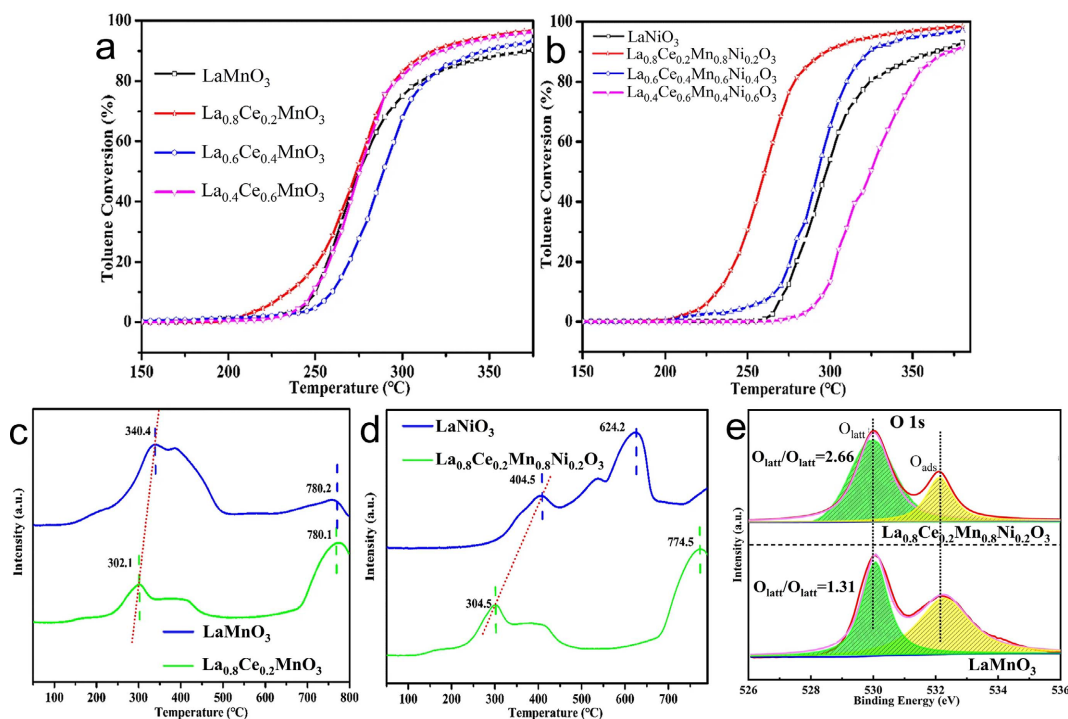


Figure 6. (a) Catalytic activity of $\text{La}_{1-x}\text{Ce}_x\text{MnO}_3$ perovskites ($x = 0, 0.2, 0.4$, and 0.6) and (b) LaNiO_3 , $\text{La}_{0.8}\text{Ce}_{0.2}\text{Mn}_{1-y}\text{Ni}_y\text{O}_3$ ($y = 0, 0.2, 0.4$, and 0.6). (c) H_2 -TPR of LMO and $\text{La}_{0.8}\text{Ce}_{0.2}\text{MnO}_3$, and (d) LaNiO_3 and $\text{La}_{0.8}\text{Ce}_{0.2}\text{Mn}_{0.8}\text{Ni}_{0.2}\text{O}_3$. (e) O 1s analysis of LMO and $\text{La}_{0.8}\text{Ce}_{0.2}\text{Mn}_{0.8}\text{Ni}_{0.2}\text{O}_3$

图 6. (a) $\text{La}_{1-x}\text{Ce}_x\text{MnO}_3$ 钙钛矿的催化活性($x = 0, 0.2, 0.4$ 和 0.6)和(b) LaNiO_3 , $\text{La}_{0.8}\text{Ce}_{0.2}\text{Mn}_{1-y}\text{Ni}_y\text{O}_3$ ($y = 0, 0.2, 0.4$ 和 0.6); (c) LMO 和 $\text{La}_{0.8}\text{Ce}_{0.2}\text{MnO}_3$ 的 H_2 -TPR; (d) LaNiO_3 和 $\text{La}_{0.8}\text{Ce}_{0.2}\text{Mn}_{0.8}\text{Ni}_{0.2}\text{O}_3$; (e) LMO 和 $\text{La}_{0.8}\text{Ce}_{0.2}\text{Mn}_{0.8}\text{Ni}_{0.2}\text{O}_3$ 的 O1s 分析

Oskoui 等人利用人工神经网络模拟了甲苯氧化催化性能与催化参数(La 的摩尔分数、Fe 的摩尔分数、煅烧温度和前驱体溶液中柠檬酸与总硝酸盐的摩尔比)之间的关系,并建立了 $\text{La}_x\text{Sr}_{1-x}\text{Fe}_y\text{Co}_{1-y}\text{O}_3$ 催化剂。双掺杂 $\text{La}_{0.9}\text{Sr}_{0.1}\text{Fe}_{0.5}\text{Co}_{0.5}\text{O}_3$ 在总转化温度(T_c) = 700°C 和 800°C, $\text{La}_{0.9}\text{Sr}_{0.1}\text{Fe}_{0.82}\text{Co}_{0.18}\text{O}_3$ 在 T_c = 700°C, $\text{La}_{0.8}\text{Sr}_{0.2}\text{Fe}_{0.66}\text{Co}_{0.34}\text{O}_3$ 在 T_c = 650°C 时实现了甲苯 100% 转化。A/B 取代对 $\text{La}_x\text{Sr}_{1-x}\text{Fe}_y\text{Co}_{1-y}\text{O}_3$ 催化剂催化性能有很大影响[78]。Li 等人采用固相研磨法制备了 $\text{La}_{1-x}\text{Sr}_x\text{Co}_{1-y}\text{Fe}_y\text{O}_3$ 钙钛矿,并对其甲苯氧化催化性能进行了评价。 $\text{La}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (LSCF)在 270°C 时表现出显著的催化活性,这是由于 A/B 位点掺杂、氧空位富集和晶格氧激活提高了氧化还原能力[79]。

2.3. 负载型钙钛矿氧化物

将贵金属纳米颗粒负载到 ABO_3 是提高其催化性能的有效方法[83]。Giraudon 等人使用氢还原煅烧法将 Pd 纳米颗粒负载到 ABO_3 表面,并研究了 Pd/LaBO₃ (B = Co, Fe, Mn 和 Ni)在甲苯氧化中的催化活性,观察到以下趋势: Pd/LaFeO₃ > Pd/LaMnO_{3-δ} > Pd/LaCoO₃ > Pd/LaNiO₃ [84]。Pd/LaFeO₃ 具有较高的甲苯氧化活性,这是由于其煅烧量较低,且无论气流性质如何,钙钛矿晶格都具有显著的高稳定性,这使得 Pt 在不同的氧化过程阶段保持相同的分散性,并且在氧化条件下保持稳定。相反,其他钙钛矿晶格的相变导致 Pt 颗粒尺寸增加,被认为是较低活性的原因。Dai 等人制备了具有链状有序大孔结构的 LaMnO₃ 和 xAu/LaMnO₃ (x = 1.4, 3.1 和 4.9 wt%),后者表面散布着 Au 纳米颗粒[85]。在复合材料中,4.9 Au/LaMnO₃ 表现出最高的催化活性,对甲苯氧化的 $T_{50\%}$ 和 $T_{90\%}$ 分别达到 201°C 和 226°C。高催化活性是由于 Au 和 LaMnO₃ 载体之间的强相互作用导致的高表面积和高负载浓度,增强了低温还原性。同样, Dai 等人制备了 3DOM $\text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$ (LSMO)及其 xAu/LSMO(x = 3.4~7.9 wt%)催化剂[86]。6.4 Au/LSMO 表现出最佳的催化活性,在空间速度(SV) = 20,000 mL·g⁻¹·h⁻¹ 时,甲苯氧化的 $T_{50\%}$ 和 $T_{90\%}$ 值分别达到 150 和 170°C。催化剂的高活性与较高浓度的表面吸附氧、良好的低温还原性以及 Au 与 LSMO 之间的强相互作用有关。Chen 等人制备了 Pd/La_{0.8}Ce_{0.2}MnO₃ 催化剂,由于 ZSM-5 载体的酸度较高,因此使用 Pd/La_{0.8}Ce_{0.2}MnO₃/ZSM-5 测试了氧化甲苯的最佳活性。Pt 在 La_{0.8}Ce_{0.2}MnO₃ 表面高度分散,样品氧化甲苯的 $T_{50\%}$ 为 112°C, $T_{90\%}$ 为 227°C [87]。Pd-LaFeO₃ 显著的催化活性在一定程度上归因于 Pd 分别在氧化和还原条件下进出钙钛矿晶格的可逆运动,有效地抑制了 Pd 的烧结和胶连。

3. 反应机理

ABO_3 氧化物催化剂作为一种优质的热催化材料,其催化降解 VOCs 的机理得到了广泛的研究。由于 VOCs 和催化剂的种类繁多,VOCs 的降解机理非常复杂。目前,VOCs 氧化存在三种主要机理: Langmuir-Hinshelwood (L-H)机理、Eley-Rideal (E-R)机理和 Mars-van Krevelen (MvK)机理[88]。MvK 机理适用于解释大多数催化剂降解反应。

3.1. Langmuir-Hinshelwood (L-H)机理

Langmuir-Hinshelwood (L-H)机理是一种多相催化过程,通过控制两个吸附分子来执行表面反应。反应分三个阶段进行:首先,将两种反应物吸附在固体催化剂上;其次,它们在表面上发生反应;最后,对产品进行解吸。吸附和解吸比表面反应快,表面反应是控制步骤。

反应速率与两种反应物在催化剂表面的覆盖率成正比。根据 L-H 模型,反应发生在吸附的 VOCs 和吸附的氧气之间。因此,VOCs 和氧气能够吸附在表面尤为重要。该模型的主要优点是它不仅考虑了反应速率,还考虑了挥发性有机化合物和氧气的吸附。L-H 机理能够解释大多数表面反应。根据 L-H 机制,吸附的 VOCs 被化学吸附的氧气(O^{2-} , O^{2-} 或 O^-)氧化成 CO_2 和 H_2O 。化学吸附的氧气是由 $\text{O}_2 \leftrightarrow \text{O}^{2-} \leftrightarrow \text{O}_2^{2-} \leftrightarrow \text{O}^-$

在氧空位周围的表面缺陷处的反应产生的[89]。

3.2. Eley-Rideal (E-R)机理

E-R 机理和 L-H 机理是使用 Langmuir 模型确定的。在 E-R 模型中, 假设气态物质 A 与气态物质 B 反应, 固体物质 S 作为催化剂。在反应过程中, A 物质首先吸附在 S 物质上, 形成类似络合物的结构, 然后 B 物质与该中间体反应得到产物。在催化剂表面, 吸附的 O_2 与气相中存在的 VOCs 发生反应。挥发性有机化合物与吸附的 O_2 之间的反应被确定为该过程的控制步骤。

3.3. Mars-Van Krevelen (MvK)机理

目前, 在催化氧化领域, MvK 机理是描述 VOCs 氧化过程的最常用手段。MvK 机理被解释为氧化还原机制。主要假设是 VOCs 与催化剂中的晶格氧反应而不是与气相中的氧气反应。MvK 的机理分为两个步骤。在初始阶段, 挥发性有机化合物扩散并吸附在催化剂表面。随后, 表面的晶格氧与 VOCs 发生反应, 形成 CO_2 和 H_2O 。同时, 催化剂内的金属氧化物也被还原。在第二阶段, 随着反应的进行, 由于气相中氧气的存在, 催化剂中先前还原的金属再次氧化成金属氧化物。MvK 反应机理的前提是反应物分子在与催化剂富氧部分反应时可以交替还原和氧化, 其中催化剂中的氧是化学吸附氧或晶格氧。Liu 等合成了 $SmMnO_3$ (SMO) 并探究了催化剂催化氧化甲苯的机理, 机理研究表明催化过程符合 MvK 机理, 甲苯的氧化依赖于吸附氧、晶格氧和氧空位的协同作用[35]。如图 7 所示, 活性氧($O^-/O_2^-/O_2^-$)从氧空位溢出, 与 VOCs 分子反应生成 H_2O 和 CO_2 。氧空位导致晶格氧的迁移, 形成吸附氧, 同时 Mn^{n+} 通过电子转移转化为 $Mn^{(n-1)+}$ 。气相氧被连续吸附到氧空位中, 将 $Mn^{(n-1)+}$ 氧化为 Mn^{n+} , 并接受来自反应物的电子形成分子吸附氧(O_2^-), 进一步转化为活性吸附氧和晶格氧, 促进 VOCs 氧化的持续发生。

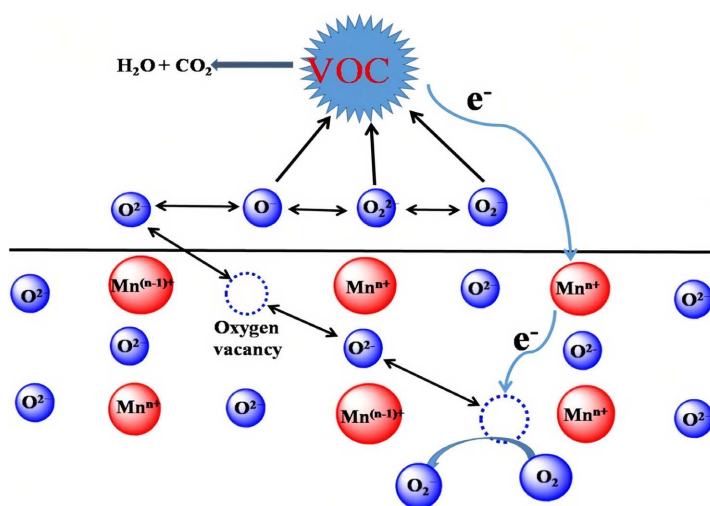


Figure 7. Possible migration and transformation mechanism of surface reactive oxygen

图 7. SMO 催化剂表面活性氧可能的迁移机理

无论是 L-H、E-R 还是 MvK 模型, 基本反应过程均可得出以下结论: 气相中的 VOCs 通过内外扩散进入催化剂表面, 最后被氧化成 CO_2 和 H_2O , 然后通过扩散返回气相。气相中 O_2 的连续流入补充了催化剂中被 VOCs 不断消耗的吸附氧。最后, 实现了完整的氧化还原反应过程, 包括吸附、降解、解吸和再生。相比之下, MvK 机理更适合解释过渡金属氧化物催化剂催化氧化 VOCs, L-H 和 E-R 模型更适合解

释贵金属降解 VOCs。目前,对中间体在降解过程中的选择性以及如何促进快速反应缺乏详细的研究,这为未来提供了潜在的研究方向。

4. 结论

催化氧化是消除 VOCs 等有机污染物的重要工艺,特别是在这些污染物浓度较低的情况下。一般来说,最活跃的催化剂是贵金属氧化物。然而,近年来,ABO₃作为氧化 VOCs 的催化剂被广泛研究,并且由于可变的成分,丰富的氧空位缺陷,高度暴露的活性表面和可调节的氧化还原性质而具有特别多用途。此外,ABO₃在 VOCs 的催化氧化中表现出较高的活性和稳定性。

ABO₃的 A 位离子(La³⁺、Ce⁴⁺、Sr²⁺、Ca²⁺等)的主要作用是稳定晶体结构。然而,通过用半径相似的离子替换 A 位阳离子可以引入晶格缺陷,改变晶格氧的化学位置,影响 B 位离子的分散性和价态,从而间接改变 ABO₃的活性。通常,ABO₃的催化活性是由 B 位离子(Co²⁺、Fe³⁺、Mn³⁺、Ni³⁺、Cu²⁺等)决定的,这些离子表现出多种氧化态,具有较好的结构和氧化还原能力。

ABO₃催化氧化 VOCs 的机理有 L-H、E-R 和 MvK 三种。ABO₃对甲苯的氧化机理主要遵循 MvK 机理,而二甲苯和 VOCs 混合物的氧化机理尚未得到充分探索,缺乏对真正烟气中含有 VOCs 的机理研究。除了 A 位点、B 位点掺杂和 A/B 位点共掺杂外, O 位点的阴离子掺杂最近已成为调整 ABO₃电子结构以提高催化性能的替代方法,需要在这个新兴领域进行进一步研究。尽管挑战依然存在,但 ABO₃有望成为实际工业中氧化 VOCs 的候选物。随着 ABO₃的不断改进,它们很可能有助于控制污染,保护健康和环境。

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